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Low Energy Metal Ion Beam Production with a Modified Freeman-Type Ion Source for Development of Novel Catalysts*

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Interactions of indium (In) and silicon (Si) atoms have been found to catalyze certain organic chemical reactions with high efficiency. In a recent paper [S. Yoshimura, *et al.*, Appl. Surf. Sci., **257**, 192 (2010)], it has been demonstrated that an In injected SiO₂ thin film formed under specific ion beam conditions catalyzes a reaction of benzhydrol with acetylacetone. In this study a technique to implant bismuth (Bi) ions into SiO₂ thin films has been developed with highly controlled ion doses and injection energies for the formation of thin films that promote Bi(III) catalysis in organic chemistry. For this purpose, the Freeman-type ion source of our beam system was modified with a new sputtering target. In addition, sticking probabilities of Bi have been obtained with the use of a quartz crystal microbalance. Although efficiency of catalytic reactions by a Bi implanted SiO₂ thin film is yet to be improved, the technique provides a Bi-Si based novel catalyst of a thin film type. [DOI: 10.1380/ejssnt.2012.139]

Keywords: Ion implantation; Bismuth; Gold; Indium; Catalysis

I. INTRODUCTION

It has been pointed out that interaction of different metal atoms such as indium (In) and silicon (Si) shows high catalytic ability [1,2]. Recently we have proposed a “physical” approach, i.e., metal ion implantation into target materials, as a technique to prepare materials that contain different metal atoms in close proximity as potential candidates for catalysts [3].

We currently attempt to develop novel catalysts by injecting metal ions such as In, gallium (Ga), and bismuth (Bi) into silicon dioxide (SiO₂) thin films formed thermally on Si substrates (which will be referred to as SiO₂/Si substrates henceforth). For this purpose, we have developed a metal ion beam production system with a low-energy mass-selected ion beam machine. In conventional experiments of metal ion beams, a solid-state metal is heated to produce liquid or gaseous metal atoms and then metal ions are produced. In this conventional method, it is necessary to install a heating system on the ion beam machine. In our ion beam system, a modified Freeman-type ion source is used, where a solid-state metal

target is used for sputtering by Ar plasmas [4]. In general, without a heating system, a sputtering method is simpler to handle as an ion source.

In an earlier study [5], we formed In injected SiO₂ films with the metal ion beam system mentioned above. It has been found that In injected SiO₂ films can catalyze an organic chemical reaction and there are optimal energy (470 eV) and dose (1×10^{17} ions/cm²) for the highest catalytic ability in the film preparation process. Dependence of In sticking probabilities on the injection energy has been also obtained. The experimental results suggest that the optimal ion energy corresponds to the sticking-probability condition that no In accumulation occurs on the substrate.

In organic chemistry, catalytic ability of Bi(III) compounds has been studied extensively as they promotes various types of chemical reactions [6]. Bi injected SiO₂ films are expected to be more effective as catalysts than In injected SiO₂ films since an inorganic Bi(III) compound generally has higher Lewis acidity than an inorganic In(III) compound. Therefore, in this study, we have developed a technique for highly controlled Bi ion injection into SiO₂ thin films using a metal ion beam production system. The quality of our Bi ion beam has been examined with a mass-and-energy analyzer. Sticking probability of Bi has been also obtained as a function of injection ion energy. In addition, in order to confirm the accuracy of our sticking probability measurement, we

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have also produced gold (Au) ions with the same ion beam system, evaluated the sticking probability of Au as a function of ion injection energy, and compared with results of earlier studies.

II. EXPERIMENTAL SETUP

Metal ion beam experiments were carried out with a low-energy mass-selected ion beam system [7]. The system consists of an ion source, an extractor electrode, a mass selector, a decelerator, and a process chamber. The configuration of the Freeman-type ion source was shown in Figs. 1 and 2 of Ref. [4]. In the Au ion production experiment, a solid-state Au was set in the ion source as a sputtering target. In the Bi experiment, we used Bi₂O₃ as a sputtering target because the melting temperature of the solid-state Bi is too low to be used as a sputtering target. The procedure of Au or Bi ion beam production is as follows: The arc chamber (25.4 mm in diameter, 50.8 mm in length) of the ion source is filled with Ar gas with a fixed gas flow rate (1 sccm). An Ar plasma is then generated by a hot tungsten wire in the arc chamber and Au or Bi atoms are sputtered from the Au or Bi₂O₃ target by Ar ion bombardment from the plasma. The target is typically biased at -500 V for efficient formation of ions. In the arc chamber, we have Ar ions, sputtered Au or Bi ions, and impurity ions. These ions are all extracted by a high voltage of -14 kV or -10 kV applied to the extractor electrode. The Au or Bi ions are then selected by a magnetic-field-based mass selector. Then Au or Bi ions are directed toward the process chamber and decelerated to the desired energy by the decelerator. The kinetic energy of the incident ion beam can be set to a desired value (ranging from 50 to 500 V for the present experiments).

In the process chamber, a Faraday cup, a substrate holder, and a gold-coated quartz crystal microbalance (QCM) (ULVAC-CRTS0) are mounted. For self-sticking probability measurement, prior to Au or Bi ion beam injection, a thin Au or Bi film was formed on a QCM crystal surface by vacuum evaporation. The thickness of the film (Au or Bi) was $0.3\ \mu\text{m}$. A mass and energy detector (balzers, PPM-421) is placed immediately behind the manipulator, on which a Faraday cup, a substrate holder, and a QCM are mounted. An ammeter (KEITHLEY-6485) is connected to the Faraday cup for the measurement of ion beam current. By moving the manipulator vertically, the Au or Bi ions can be injected to the Faraday cup, the substrate holder, or the QCM crystal, selectively. The ion beam can be also injected into the PPM-421 by moving the manipulator to the uppermost position, so that the manipulator does not obstruct the ion beam path. The degree of vacuum in the process chamber was about 10^{-9} Torr.

The sticking probability is the ratio of the number of deposited atoms to that of incident ions. The number of incident ions can be obtained from the ion beam current measured by the Faraday cup. The number of deposited atoms can be evaluated from the change in mass of the Au or Bi thin film formed on the QCM crystal surface. The QCM crystal is a gold-coated AT-cut crystal and has a resonant frequency of 5 MHz. The film mass change on the QCM crystal can be monitored by a QCM controller

(ULVAC-CRTM9000). The mass resolution of the QCM system is 2.4×10^{-11} g. With this QCM system, we have measured sputtering yields of Au [8] and magnesium oxide (MgO) [9, 10] by He, Ne, Ar, Kr, or Xe ion beams and found that the measured sputtering yields agree well with earlier data obtained by other experimental groups.

In this study, the experimental procedure is as follows. Firstly, we measure the mass spectrum of a plasma in the ion source by varying the current to generate the magnetic field of the magnetic-field-based mass selector. Secondly, with an appropriate adjustment of the mass selector, Au or Bi ion beams are selected and their mass and energy distributions are measured by PPM-421. Before the QCM measurement, the ion beam is injected into the Faraday cup to measure the number of incident ions. Then, the Au or Bi ion beams are injected into Au or Bi films formed on QCM crystals, with which the number of deposited Au or Bi atoms is measured. Finally, the ion beam current is measured again to confirm that it has not changed during the measurement. With these data, sticking probabilities of Au and Bi can be estimated for each ion beam injection energy.

For the subsequent experiments, a SiO₂/Si substrate was set on the substrate holder. The thickness of a SiO₂ layer of the substrate was about $0.1\ \mu\text{m}$. The Bi ion beams were injected into the substrates with different energies. Once Bi injected SiO₂/Si substrates were formed in this manner, the surface condition of each SiO₂/Si substrate was first analyzed by atomic force microscopy (AFM). Then catalytic abilities of Bi injected SiO₂/Si substrates were finally examined.

III. RESULTS AND DISCUSSION

A. Au ion beam experiment

Firstly, we measured the mass spectrum of a plasma in the ion source for Au ion beams. By changing the electric current of the mass selector, ions extracted from the ion source was measured by the Faraday cup. Figure 1(a) shows the dependence of ion beam intensity on the mass selector current. In Fig. 1(a), several ion peaks are seen, which are identified by PPM-421 as C⁺, N⁺, O⁺, Ar²⁺, N₂⁺, Ar⁺, W⁺, and Au⁺ ions. Identification of other peaks was difficult because the ion currents for these peaks were too low.

With an appropriate adjustment of the current in the magnetic-field-based mass selector, we selected a specific ion beam. The mass spectrum of a mass-selected ion beam was measured by PPM-421, which is shown in Fig. 1(b). Figure 1(b) indicates that only a single peak appears at the mass number of 197, i.e., Au⁺ ions with no impurity. An example of the energy spectrum measured by PPM-421 is given in Fig. 2, which shows that, in this specific case, the peak energy is 207 eV and the full width at half maximum (FWHM) of the energy distribution is 7 eV. These results show that the mass-selected Au ion beam used in this study was nearly monochromatic.

In Fig. 3, measured sticking probabilities of Au are shown by closed squares. The horizontal axis represents the peak energy of ion beam determined by PPM-421. Figure 3 shows that the sticking probability decreases

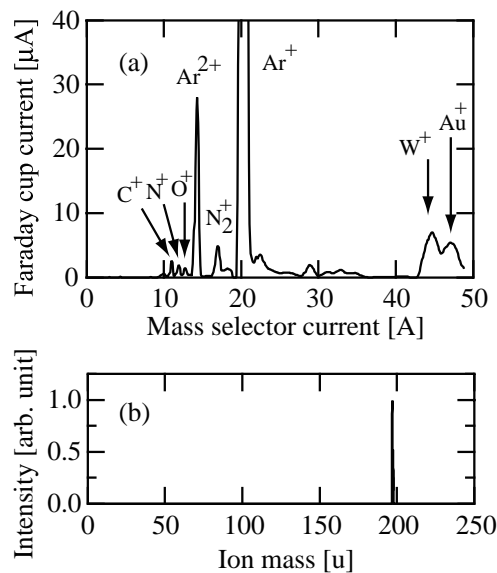


FIG. 1. (a) Ion beam intensities measured by the Faraday cup for each ion species selected by the magnetic mass selector. The horizontal axis represents the current to produce the magnetic field of the mass selector. The figure shows the mass spectrum of ions in the ion source. (b) Mass spectrum of a mass-selected ion beam used in the study. The peak mass number is 197, which corresponds to the mass of Au.

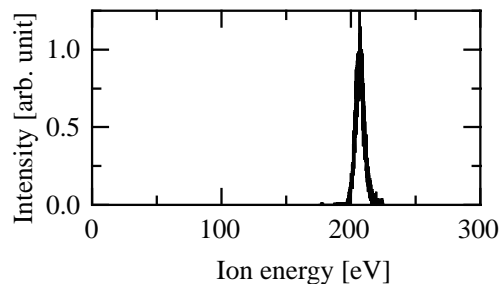


FIG. 2. An example of energy spectrum of a Au ion beam used in this study.

monotonically with increasing ion energy and becomes almost zero at the ion energy of about 200 eV. It is also seen that the sticking probability becomes negative in the energy range of 200–500 eV, indicating that the Au substrate is sputtered by the injected Au ion beam (self-sputtering) in this energy range. In previous papers [11, 12], self-sputtering yields of Au measured by other experimental groups were presented. The sticking probabilities of Au can be deduced from the self-sputtering yields by a simple relation between the self-sputtering yield Y and the sticking probability P with $Y = 1 - P$. In Fig. 3, the sticking probabilities of Au obtained from [11] and [12] are also plotted by open triangles and open circles, respectively. Figure 3 shows that the measured sticking probability agrees with those in Ref. [11] and our preliminary measurement [13], however, are inconsistent with those in Ref. [12].

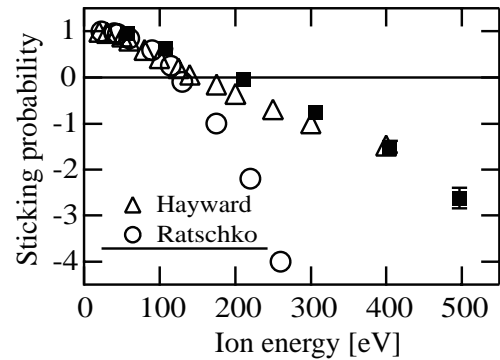


FIG. 3. The measured sticking probabilities of Au versus the ion injection energy are shown by closed squares. The angle of incidence is normal to the Au film on the QCM crystal surface. The error bar indicates the standard deviation of the measured data for each incident energy. The previous data in Refs. [11] and [12] are shown by open triangles and open circles, respectively.

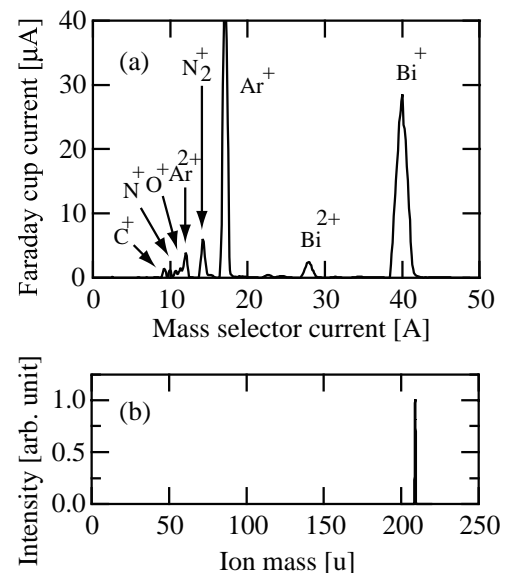


FIG. 4. (a) Ion beam intensities measured by the Faraday cup for each ion species selected by the mass selector. The horizontal axis represents the current to produce the magnetic field of the mass selector. The figure shows the mass spectrum of ions in the ion source. (b) Mass spectrum of a mass-selected ion beam used in the study. The peak mass number is 209, which corresponds to the mass of Bi.

B. Bi ion beam experiment

Figure 4(a) shows the mass spectrum of ions extracted from the ion source for a Bi ion beam. It was found that C^+ , N^+ , O^+ , Ar^{2+} , N_2^+ , Ar^+ , Bi^{2+} , and Bi^+ ions were present in the ion source. The mass spectrum of a mass-selected ion beam was measured by PPM-421, which is shown in Fig. 4(b). Figure 4(b) indicates that only a single peak appears at the mass number of 209, which corresponds to that of Bi^+ ions. An example of the energy spectrum measured by PPM-421 is given in Fig. 5, which shows that, in this specific case, the peak energy is 205

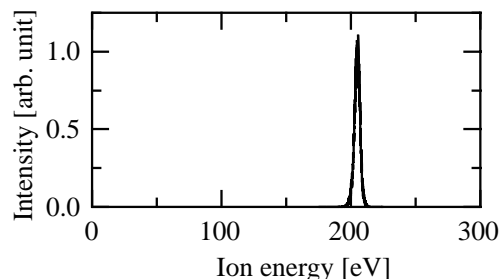


FIG. 5. An example of energy spectrum of Bi ion beam used in this study.

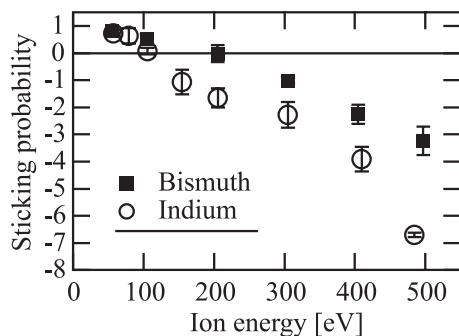


FIG. 6. The measured sticking probabilities of Bi versus the ion injection energy are shown by closed squares. The angle of incidence is normal to the Bi film on the QCM crystal surface. The error bar indicates the standard deviation of the measured data for each incident energy.

eV and the FWHM of the energy distribution is 5 eV.

As far as we know, sticking probabilities of Bi have not been reported yet. We have measured sticking probabilities of Bi using the ion beam and the QCM system. In Fig. 6, measured sticking probabilities of Bi are shown by closed squares, which indicate that the sticking probability decreases monotonically with increasing ion energy and becomes negative in the energy range of 200–500 eV. The measured sticking probabilities of Bi are similar to those of Au (Fig. 3). For comparison, the measured sticking probabilities of In [5] are also plotted in Fig. 6 by open circles. It is seen that the sticking probability of In also monotonically decreases with increasing ion energy. Especially, for ion energy larger than around 100 eV, self-sputtering is shown to take place.

Following the experiments discussed above, Bi ion beams were injected into SiO₂/Si substrates. Two Bi injected SiO₂/Si substrates were prepared. The Bi ion beam current used in the experiments was about 2 μ A. The size of the substrate was approximately 1cm \times 1cm and the area exposed to the ion beam was a disk with a diameter of 0.8 cm. The ion energies were (a) 200 and (b) 470 eV. The ion doses were (a) 1.2×10^{17} ions/cm² and (b) 1.5×10^{17} ions/cm², respectively.

The surfaces of the Bi injected substrates (a) and (b) mentioned above were analyzed by AFM, photographs of which are given in Fig. 7. Figure 7 shows that the substrate surface morphology after Bi ion injection depends on the ion energy. In (a) and (b) of Fig. 7, particle-like structures are seen. Cross section profiles of the surfaces

along the solid lines of (a) and (b) are given in (c) and (d) of Fig. 7.

C. Evaluation of catalytic reactions by Bi injected SiO₂

Catalytic ability of the Bi injected SiO₂ thin films was examined for a reaction of benzhydrol with acetylacetone, which has been found to be promoted by catalytic effects of In injected SiO₂ thin films [3]. The organic chemical reactions were examined in a 10 mL flame-dried two necked round-bottomed flask equipped with a stop cock, a Teflon-coated magnetic stirring bar, and a reflux condenser fitted with nitrogen inlet adapter. A Bi injected SiO₂/Si substrate was broken into 5–10 small species and placed in the flask, together with benzhydrol (1 mmol), acetylacetone (1.2 mmol), and toluene (2 mL). The resulting mixture in the flask was heated at 80 $^{\circ}$ C in an oil bath for reaction periods of 21 hours. After the reaction, the mixture was cooled to room temperature and treated with H₂O (10 mL) and diethyl ether (10 mL). The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give the crude product. Reaction yields were determined by ¹H NMR using the internal standard.

Figure 8 shows the reaction results for the SiO₂/Si substrates with Bi ion injection. The percentage shown here is the molar distribution. As denoted in Fig. 8, the reaction of benzhydrol (1) and acetylacetone (2) here produces the coupling product (3) and bis(diphenylmethyl) ether (4). In an earlier paper [5], we have injected In ions to SiO₂/Si substrates. When the ion energy was 470 eV and the ion dose was 1×10^{17} ions / cm², the coupling product and bis(diphenylmethyl) ether were obtained in 6% and 38% yields, which clearly showed the catalytic effect. By contrast, when the Bi ions were injected to the SiO₂/Si substrate, the yields of the coupling product and bis(diphenylmethyl) ether were null and benzhydrol was fully recovered, as shown in Figs. 8(a) and 8(b). Although the ion energy and ion dose of the substrate [Fig. 8(b)] is similar to that of In injected substrate [5], no significant reaction was observed in the case of Bi injected SiO₂/Si substrates in their energy and dose ranges examined here.

In the study of Ref. [5] and recent additional experiments, we have found that the sticking probability measurement is helpful for the estimation of the optimal ion energy for catalytic ability. For the substrates created with In ion energies of 50, 100, 200, and 400 eV and with an In ion dose of 1×10^{17} ions/cm², the yields of the coupling product and bis(diphenylmethyl) ether were null whereas benzhydrol was nearly fully recovered. On the other hand, the coupling product and bis(diphenylmethyl) ether were obtained when the In ion energy was 470 eV and the In ion dose was 1×10^{17} ions/cm². Figure 6 suggests that metallic In surface layers are likely to be formed in the cases of 50 and 100 eV. Therefore it is conceivable that surfaces of the substrates with 50 or 100 eV injections consist of In films and the surface In atoms lack interactions with Si atoms which are necessary for the catalytic effect. Since metallic In alone does not catalyze

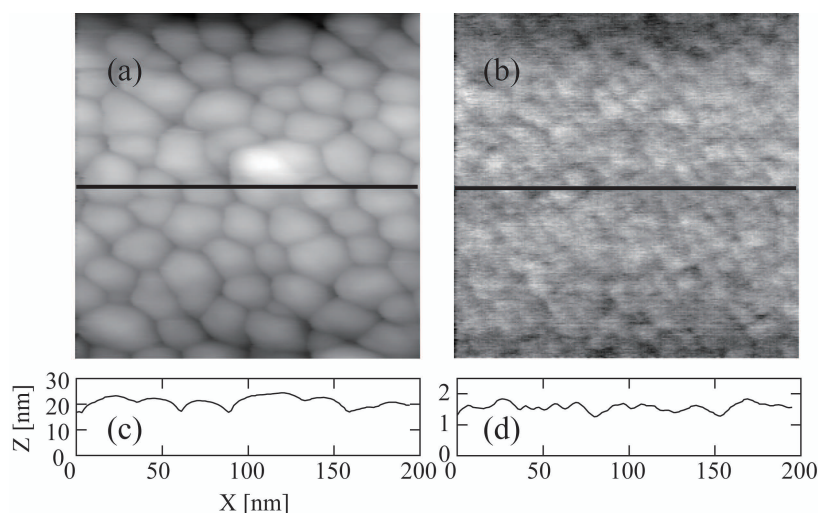


FIG. 7. Atomic force microscopy (AFM) images of Bi injected SiO_2/Si substrate surfaces. The injection ion energies are (a) 200 and (b) 470 eV. Cross section profiles of the surfaces along the solid lines of (a) and (b) are given in (c) and (d).

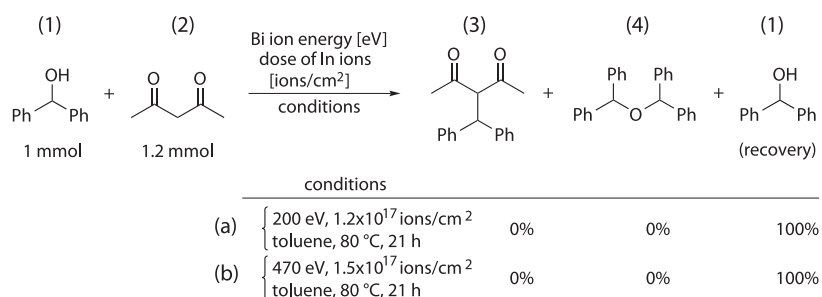


FIG. 8. Yields of benzhydrol and acetylacetone reactions with Bi injected SiO_2/Si substrate catalysis.

the organic chemical reaction [3], these substrates do not catalyze the reactions. For the substrates with 200, 400, and 470 eV injections, on the other hand, In ions are likely to be implanted into the subsurface regions of SiO_2 films as the ion energy is high enough that no In deposition takes place. Although, in the case of In injection, the reason why the substrates with 200 and 400 eV injections do not catalyze the reactions has not been clear yet, the experimental observations suggests that the threshold ion incident energy for manifestation of the catalytic effect exists between 400 and 470 eV.

Figure 6 also shows that the self-sputtering yields of Bi in the range of 200-500 eV are much smaller than those of In. These results suggest that the reason why no significant reaction was observed in the case of Bi injected SiO_2/Si substrates in their energy and dose ranges examined here is that the Bi ion energy in this study is too low to catalyze the reaction.

IV. CONCLUSIONS

We currently attempt to develop novel catalysts by injecting metal ions into SiO_2 thin films. For metal ion beam production, the Freeman-type ion source of our low-energy ion beam machine was modified to hold a sputtering target in the arc chamber of the ion source. In this

study, ions generated in the ion source were accelerated and then mass selected to produce a pure ion beam (in this study, Au or Bi ions). The ion beam was then decelerated and injected into the substrate with a desired injection energy in the range of 50-500 eV. The quality of the ion beam was examined by PPM-421. It was confirmed that the ion beam included no impurity ions and the energy distribution was nearly monochromatic. The measurement system for sticking probability was also established and installed in the low-energy ion beam system. The sticking probabilities of Au and Bi were found to decrease monotonically as the ion energy increases. It has been also found that the incident Au or Bi ions deposit on the substrate if the ion energy is 200 eV or less and that the Au or Bi atoms are sputtered from the substrate if the energy is higher than 200 eV. The Bi ion beam was injected into a SiO_2 thin film to create a material that has both Bi and Si in close proximity, which may become a new type of Bi(III) catalyst in organic chemistry. Contrary to the In injected SiO_2 thin film [5], our study on the catalytic abilities shows that no catalytic effect is observed in their energy and dose ranges examined here. However, we think that the metal ion beam injection technique developed in this study is useful in developing a catalyst of a thin-film type with highly controlled ion beam doses and injection depths into the substrate.

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